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Correlation of Energy Levels of Linear and Bent Triatomic Molecules, and the Ultraviolet CS_2 Absorption Spectrum

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A set of vibronic levels for a ${}^1\Sigma^+{}_g$ and a ${}^1\Pi_g$ electronic state of linear AB_2 is shown in a diagram, together with gyrovibronic levels of the corresponding electronic states (a ${}^1A_1$ and a ${}^1B_2$ and a ${}^1A_2$) of bent AB_2; and a correlation is set up between the sets of gyrovibronic levels of the two cases. This diagram is then used in a discussion of the near-ultraviolet absorption bands of carbon disulfide, where the molecule is linear in the ${}^1\Sigma^+{}_g$ ground state. The band types and structures for such a transition are discussed; the structures should be practically identical in character whether the upper state is linear or bent. Vibrational intensities, and their relation to a strong allowed electronic transition at shorter wave-lengths, are also discussed. It is concluded that the near-ultraviolet system is an electronic-allowed transition to a ${}^1B_2$ bent molecule upper state related to a ${}^1\Pi_g$ linear molecule state.

I. CORRELATION OF GYROVIBRONIC STATES OF LINEAR AND BENT AB_2

IN a preceding paper,[1] the species classification and rotational energy level patterns of non-linear triatomic molecules AB_2 have been discussed. If, for any such molecule, we imagine the ABA apex angle to be increased continuously to 180°, the energy level system must go over somehow into that of linear AB_2. Since, however, the type of electronic and vibrational quantization is very different in the two cases, it is evident that in the transition region radical and complicated transformations must occur in the wave functions and in the arrangement of levels. In the first three sections of this paper, the matter of bridging this region is considered by using a qualitative correlation scheme relating the energy level patterns of linear and bent AB_2. In the last section, electronic transitions from *linear* to *linear or bent* molecular states, and their band structures, are considered, and the results are applied to the interpretation of the near-ultraviolet absorption spectrum of carbon disulfide.

If the bending of any AB_2 molecule is small or moderate,[1] the rotation approximates rather closely to that of a symmetric top, with quantum number K_η for the rotation about the least moment of inertia axis η. K_η becomes an increasingly good quantum number with approach to linearity. At the same time, however, a strong vibration-rotation interaction must set in, essentially between the deformation vibration mode ν_2 and the K_η rotation, whose quanta become larger and larger as the molecule straightens out and the moment of inertia I_η decreases. This interaction points toward the situation in linear AB_2, where there is a two-dimensional vibration mode ν_2 with quantum numbers v_ρ (radial) and l (azimuthal).

At the same time, strong electronic-rotational interactions may develop, leading to an electronic angular momentum around the axis with quantum number Λ. In the linear molecule, K is in general the sum of Λ and l. During the change from bent to linear AB_2, we normally expect K_η to become K, although since K_η is not quite rigorous, occasional deviations from this correlation are possible.

Linear AB_2, like diatomic B_2, is a prolate symmetrical-top rotator, but, because of the zero equilibrium moment of inertia around the symmetry axis, the wave functions and energy level patterns differ considerably from those of non-linear symmetrical top molecules. In particular, $K>0$ is possible in linear molecules only by the excitation of vibronic angular momentum (i.e., Λ and/or l), and K here forms an integral part of the vibronic as well as of the rotational species classification.

The wave functions reflect these differences. Thus we have:[1]

Moderately bent AB_2, $\psi_{evr}=\psi_r\psi_{ev}+\psi'_{evr}$,
with

$$\psi_r\approx S_{JKM}=2^{-\frac{1}{2}}(\overset{\times}{\psi}_{JKM}+(-1)^\gamma\overset{\times}{\psi}_{J-KM}), \qquad (1)$$

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[1] R. S. Mulliken, Phys. Rev. 59, 873 (1941).

but

Linear AB_2,

$$\psi_{evr}=2^{-\frac{1}{2}}(\overset{\times}{\psi}_{JKM}\overset{K}{\psi}_{ev}+(-1)^{\delta}\overset{\times}{\psi}_{J-KM}\overset{-K}{\psi}_{ev}), \qquad (2)$$

with $\delta=0$ or 1. (Recall that $K=|k|$, so that $+K$ and $-K$ represent two values of k differing in sign only.) It is characteristic of linear AB_2 that the combination of $k=+K$ and $k=-K$ cannot occur until the ψ_{evr} stage, instead of within the ψ_r factor as in bent AB_2. Thus for linear AB_2 no rotational functions S_{JKM} classifiable under asymmetric-top species exist as they do[1] for bent AB_2.

In Section V of the preceding paper[1] the concept of gyrovibronic species was defined for moderately bent AB_2; this corresponds to gyrovibronic wave functions

$$\psi_{evk}=(2\pi)^{-\frac{1}{2}}e^{ik\phi}\psi_{ev}, \qquad (3)$$

the factor $(2\pi)^{-\frac{1}{2}}e^{ik\phi}$ having been borrowed from the rotational function ψ_{JkM}. There are two wave functions ($k=\pm K$) for each gyrovibronic state; in the complete ψ_r or ψ_{evr}, these are combined as in Eq. (1) and give rise to K doubling. Similarly for linear AB_2,

$$\psi_{evk}=(2\pi)^{-\frac{1}{2}}e^{ik\phi}\overset{k}{\psi}_{ev}; \qquad (4)$$

here ψ_{evk} really differs from $\overset{k}{\psi}_{ev}$ only in the way of measuring the internal angular coordinates ϕ_i. The ϕ_i are part of a set of cylindrical coordinates for the electrons and nuclei; this type of coordinates is especially convenient for linear molecules. Let the top axes x, y, z be chosen to coincide, respectively, with ζ, ξ, η of Fig. 3 of the preceding paper[1] (A nucleus in xz plane), and let ϕ be measured from the line of nodes to the x axis. Further, let a ϕ_i be similarly defined for each electron. If also we define the *relative* coordinates $\Phi_i=\phi_i-\phi$ for the electrons, then ψ_{evk} in Eq. (4) is a function of the ϕ_i's and $\overset{k}{\psi}_{ev}$ is the corresponding function of the Φ_i's.

Because of this simple relation between ψ_{evk} and $\overset{k}{\psi}_{ev}$, the gyrovibronic species classification for linear AB_2 is identical with the vibronic species classification. The latter, in turn, is formally the same as the electronic species classification for symmetrical diatomic molecules, being based, like the latter, on the symmetry group $D_{\infty h}$. We can, therefore, conveniently adopt the well-known diatomic species definitions and symbolism: Σ, Π, Δ, etc., for $K=0$, 1, 2, etc. (K in the diatomic case is called Λ), with subscript g or u to denote behavior under inversion of the internal axis-system x, y, z, and superscript $+$ or $-$ for Σ states to denote behavior for reflection of the axis-system in any plane through the symmetry axis. To distinguish electronic, vibrational, and vibronic species, one can, if necessary, add a superscript e, v, or ev at the left of the species symbol: for example, ${}^{e3}\Sigma^{+}{}_{g}$, ${}^{v}\Sigma^{+}{}_{g}$, ${}^{ev3}\Sigma^{+}g$.[2]

For moderately bent AB_2, a gyrovibronic species classification is obtained by merely giving K value and vibronic species.[1] Each gyrovibronic species of bent AB_2 shows a characteristic pattern with respect to over-all species character of rotational levels as a function of J; and comparison with the similar sets of level patterns for linear AB_2 leads to the setting up of a correspondence between the gyrovibronic species of bent and linear AB_2.[3] This correspondence, already embodied in Fig. 6 of the preceding paper,[1] furnishes the desired scheme for qualitatively bridging the gap between the energy levels of linear and bent AB_2. As the figure shows, there is a one-to-one correspondence for $K=0$, a two-to-one correspondence (two gyrovibronic species of bent AB_2 to one of linear AB_2) for $K>0$.

It may be noticed that gyrovibronic species such as Π_u, Φ_u (or any odd K) have qualitatively identical over-all species patterns in Fig. 6 of the preceding paper; similarly with sets like Δ_g, Γ_g. The members of such a set are distinguished only by their K values. Since, however, the K classification is not quite a rigorous property of ψ_{evr}, especially for bent AB_2, perturbations may occur between members of any such set; and if two gyrovibronic levels belonging to one set tend to cross during a correlation, this crossing will, technically though usually not in a practical sense, be avoided.

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[2] Cf. R. S. Mulliken, J. Phys. Chem. **41**, 159 (1937).

[3] The over-all species patterns for various electronic states of symmetrical diatomic molecules are well known (cf., e.g., G. Herzberg, *Molecular Spectra and Molecular Structure. I. Diatomic Molecules* (Prentice-Hall, 1938), pp. 261–2). It is easily seen that exactly the same patterns must occur for like-named electronic states of linear AB_2, and, further, for like-named vibronic states of linear AB_2.

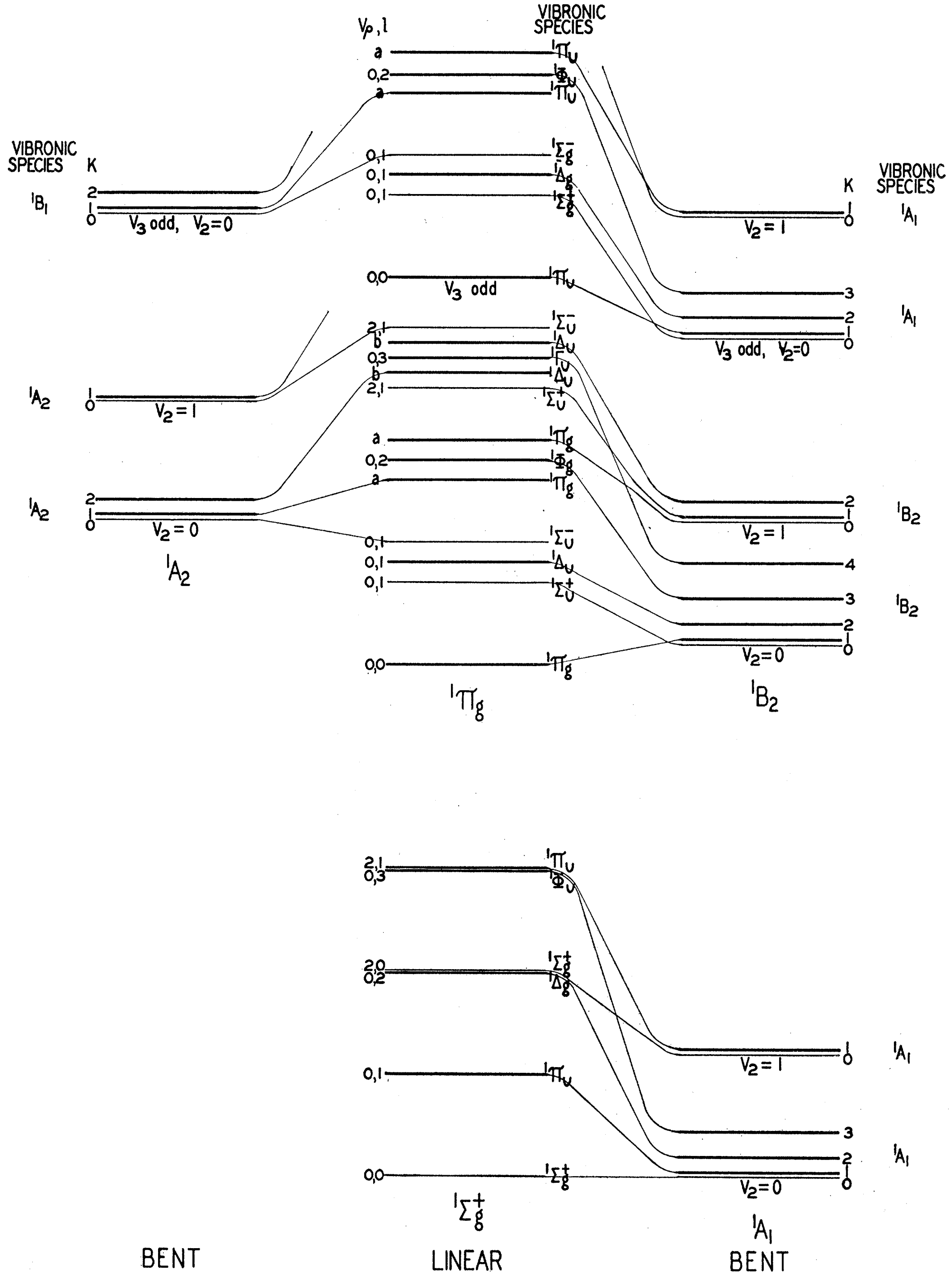

FIG. 1. Correlation between (gyro)vibronic levels of a ${}^1\Sigma_g{}^+$ and a ${}^1\Pi_g$ electronic state of linear AB_2 (middle section of diagram) and gyrovibronic (i.e., vibronic and K) levels of corresponding electronic states (${}^1A_1$, ${}^1A_2$ and ${}^1B_2$) of bent AB_2 (outer sections of diagram). The diagram covers various states of excitation of the deformation frequency (quantum numbers v_ρ and l in linear AB_2, v_2 in bent AB_2). It assumes no excitation of the antisymmetrical frequency (quantum number v_3), except at the top of the diagram; and it ignores additional levels, and other complications, corresponding to excitation of the symmetrical valence frequency. For the levels marked a and b, definite v_ρ, l values cannot be given; a refers to levels whose wave functions are mixtures of 2, 0 and 0, 2, b to mixtures of 0, 3 and 2, 1. Each "level" of Fig. 1 represents actually a whole set of rotational levels, whose characteristics can be obtained by reference to Fig. 6 of reference 1. (A slight error has been made in the drawing in that the correlation lines coming from the left to the levels $K=0$ and 1 of $v_2=1$ of the ${}^1B_2$ state *should cross.*)

Still more generally, $\Sigma^+{}_u$ and $\Sigma^-{}_u$ can perturb Π_u states, Π_u can perturb Δ_u, $\Sigma^+{}_g$ and $\Sigma^-{}_g$ can perturb Π_g, and so on. In general, however, these effects should be no larger than ordinary perturbations in diatomic spectra. Between levels belonging to g and u gyrovibronic species, no appreciable interactions can occur.

II. VIBRATIONAL AND VIBRONIC STATES OF LINEAR AB$_2$

Before proceeding further, it is desirable to review the modes of vibration of linear AB$_2$. These may be classified, like the ψ_{evk}'s, as species of the group $D_{\infty h}$, where however, small instead of capital letters are used for the species symbols.[2] There are the symmetrical mode ν_1, species σ_g, the antisymmetrical mode ν_3, species σ_u, and the degenerate pair of deformation modes ν_2, species π_u. The two deformation degrees of freedom are best taken as a radial and an azimuthal, with quantum numbers v_ρ and l $(v_\rho+|l|=v_2)$. The possible values of v_ρ and $|l|$ for a given v_2 are $v_\rho=0$, $|l|=v_2$; $v_\rho=2$, $|l|=v_2-2$; and so on.

For the complete ψ_v, the species is respectively $\Sigma^+{}_g$, Π_u, Δ_g or Φ_u according as $|l|=0, 1, 2,$ or $3\cdots$. if v_3 is even; for v_3 odd, the g and u subscripts are reversed. If the electronic state ψ_e is ${}^1\Sigma^+{}_g$, then the ψ_{evk} species is the same as the vibrational species, except for addition of the multiplicity symbol. Figure 1 (lowest section of middle column) shows the vibronic levels and their species symbols for a ${}^1\Sigma^+{}_g$ electronic state with $v_3=v_1=0$ but v_2 ranging from 0 to 3.

In general, if we let $\pm\Lambda h/2\pi$ represent (as in the diatomic case) the *electronic* orbital angular momentum around the symmetry axis, the total orbital angular momentum $kh/2\pi=\pm Kh/2\pi$ around this axis is given by

$$K=|\Lambda+l|. \tag{5}$$

Taking K and Λ as always positive, it is necessary to let l in Eq. (5) assume either positive or negative values, the $+$ sign when the l vector is parallel to $\pm\Lambda$, the $-$ sign when it is antiparallel. For a given Λ and $|l|$, there are, in general, two K values $\Lambda+|l|$ and $|\Lambda-|l||$, each (if $K\neq 0$) having a pair of wave functions obtained from $\delta=0$ and $\delta=1$ in Eqs. (2).

The vibronic states resulting from the combination of any given type of electronic and vibrational state can be determined, since ψ_e, ψ_v, and ψ_{evk} species are all classified under $D_{\infty h}$, by species multiplication according to well-known group-theoretical procedure. The vibronic levels are illustrated in the middle section of the middle column of Fig. 1 for a ${}^1\Pi_g$ electronic state with $v_1=0$ and $v_3=0$ (or an even number), and v_2 ranging from 0 to 3. Above, in the top section, are illustrated a further set of vibronic levels for $v_3=1$ (or any odd value). The vibronic levels in the middle section of Fig. 1 are spaced approximately like those of an actual linear AB$_2$ molecule, except that certain levels with $v_1>0$, which actually would come in the energy ranges covered, are omitted. In practice, these would cause marked complications (the reader may recall the well-known perturbations in CO$_2$ resulting from the approximate equality of $2\nu_2$ and ν_1).

For each value of $v_2>0$, there are two or more vibronic levels. These differ very little in energy if $\Lambda=0$ and if there is no perturbation by excited v_1 levels. If $\Lambda=1$, the Renner effect should, in general, cause relatively large energy differences between the different levels for a given v_2,[4] and the ${}^1\Pi_g$ levels in Fig. 1 have been drawn in qualitative accordance with this expectation.

III. CORRELATION OF LEVELS OF LINEAR AND BENT AB$_2$

We now have, in Fig. 1, typical sets of gyrovibronic levels for two different types of electronic states of linear AB$_2$, and wish to correlate these with corresponding levels of bent AB$_2$. Before doing this, two steps remain: (a) to determine what relations exist between electronic species of linear and bent AB$_2$; (b) to add to

TABLE I. *Correlation of electronic states of linear* AB$_2$ *(symmetry $D_{\infty h}$) with those of bent* AB$_2$ *(symmetry C_{2v}). Cf. reference 5 regarding the derivation.*

LINEAR AB$_2$	BENT AB$_2$	LINEAR AB$_2$	BENT AB$_2$
$\Sigma^+{}_g$	A_1	Π_u, Δ_g, or Φ_u	A_1+B_1
$\Sigma^-{}_g$	B_1		
$\Sigma^+{}_u$	B_2	Π_g, Δ_u, or Φ_g	A_2+B_2
$\Sigma^-{}_u$	A_2		

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[4] R. Renner, Zeits. f. Physik **92**, 172 (1934).

Fig. 1 gyrovibronic levels of the proper bent AB_2 electronic states.

If we consider the electronic wave functions by themselves, as if the nuclei were fixed, the way in which the various species of electronic states of linear AB_2 go into those of bent AB_2 can be determined by familiar methods,[5] with results as given in Table I. Thus the ${}^{e1}\Sigma^+{}_g$ state of linear AB_2 corresponds to an ${}^{e1}A_1$ state of bent AB_2, while the ${}^{e1}\Pi_g$ state must split into an ${}^{e1}A_2$ and an ${}^{e1}B_2$ state, the magnitude of the splitting increasing with the bending.

Gyrovibronic levels for bent AB_2 corresponding to those shown for linear AB_2 have been drawn at the left and right of Fig. 1. For each vibrational state shown, a few gyrovibronic levels have been added, spaced according to CK^2. The spacings of the vibrational levels of both bent and linear AB_2 in Fig. 1 have been chosen so as to be related roughly as for an actual molecule like CO_2 or NO_2. Levels with $v_1>0$ have been omitted for the sake of simplicity for bent AB_2 just as for linear AB_2.

By using Fig. 6 of the preceding paper,[1] correlation lines can now be drawn connecting corresponding gyrovibronic states of linear and bent AB_2 in Fig. 1. The results are interesting. If we look first at the ${}^{e1}\Sigma^+{}_g$ state and correlate with ${}^{e1}A_1$, Fig. 1 shows a systematic correlation of vibrational levels in such a way that v_2 (bent AB_2) $=\frac{1}{2}v_p$ (linear AB_2).

On considering the ${}^{e1}\Pi_g$ state, for $v_3=v_1=0$ (similar results are expected for $v_1>0$, $v_3=$even), some of the gyrovibronic levels are found to connect with those of ${}^{e1}B_2$, others with those of ${}^{e1}A_2$. It is particularly interesting that the two lowest vibrational levels of ${}^{e1}\Pi_g$ cross each other in going over to the lowest two K levels of ${}^{e1}B_2$. In particular, the ${}^{e1}\Pi_g$ level with $v_3=v_1=v_2=0$, where $K=1$ is purely electronic angular momentum, goes over into the second K level of $v_3=v_1=v_2=0$ of ${}^{e1}B_2$, where $K=1$ is purely nuclear top angular momentum. K is conserved, but the carrier of the angular momentum changes completely, and the wave function must be radically transformed. A detailed study of the changes in the gyrovibronic wave functions in the correlation between ${}^{e1}\Pi_g$ and ${}^{e1}A_2$ plus ${}^{e1}B_2$ shows several types of interesting transformations, but these will not be discussed here. For the vibrational wave functions also, radical changes have to occur, as is shown by the rule v_2 (bent) $=\frac{1}{2}v_p$ (linear), which holds in the same way here as for the ${}^{e1}\Sigma^+{}_g$ state.

When levels with $v_3=1$ are considered, a correlation rule v_3 (bent) $=v_3$ (linear) is seen to be fulfilled. It is apparent also that there is a tendency for v_1 (bent) $=v_1$ (linear), but that this must be modified in practice by strong interactions between excited v_1 and v_p levels (linear AB_2) or between v_1 and v_2 levels (bent AB_2). These interactions must also, in practice, interfere more or less with the smoothness of the correlations v_2 (bent) $=\frac{1}{2}v_p$ (linear). For strongly vibrating states, many vibrational interferences of various sorts will enter to upset the simplicity of the correlations.

Although Fig. 1 shows directly only the correlation behavior for ${}^{e1}\Sigma^+{}_g$ and ${}^{e1}\Pi_g$ states of linear AB_2, it illustrates how these may be constructed in general.

IV. SELECTION RULES AND BAND STRUCTURES FOR ELECTRONIC TRANSITIONS FROM LINEAR AB_2 TO LINEAR OR BENT AB_2 STATES; WITH APPLICATIONS TO THE ULTRAVIOLET CARBON DISULFIDE ABSORPTION SPECTRUM

In the ultraviolet absorption spectrum of carbon disulfide vapor there is a region near λ3000 containing a great number of bands. The molecule is linear in the lower electronic state, which is ${}^1\Sigma^+{}_g$.[6] If it were linear in both states, not more than one series of bands of any considerable intensity would be expected, but the large number of observed bands can be understood if we use the Franck-Condon principle and if the equilibrium configuration of the molecule is non-linear in the upper state. A study of the electronic structures of CO_2, CS_2 and related molecules makes it rather probable that the latter is a ${}^1\Pi_g$ state if the molecule is linear;[6] if it is bent, this ${}^1\Pi_g$ should be replaced by two corresponding states, a ${}^1A_2$ and a ${}^1B_2$ (cf. Table I), perhaps

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[5] Cf. R. S. Mulliken, Phys. Rev. **43**, 293 (1933), Table III. Although the results now needed are not given (cf. footnote *a* of the table), they can be obtained by the method given there.

[6] R. S. Mulliken, J. Chem. Phys. **3**, 739 (1935).

TABLE II. *Survey of permitted gyrovibronic transitions for a transition between an* ${}^e\Sigma^+_g$ *and an* ${}^e\Pi_g$ *state of linear* AB_2, *and between* ${}^e\Sigma^+_g$ *of linear and* ${}^eB_2$ *and* ${}^eA_2$ *of bent* AB_2. *(*${}^eB_2$ *and* ${}^eA_2$ *of bent correspond to* ${}^e\Pi_g$ *of linear* AB_2*—see Table I.) Only the transitions marked in bold-face type are allowed by electronic selection rules. Polarization: p means perpendicular, (ξ and ζ), η parallel, to the axis of linear* AB_2 *(axes ξ, η, ζ as in Fig. 3 of reference 1). In the first two sections of the table,* Σ^+_g *and so on indicate (gyro)vibronic states.*

			${}^e\Pi_g$										${}^eB_2$								${}^eA_2$							
			EVEN v_3					ODD v_3					EVEN v_3; $K=$				ODD v_3; $K=$				EVEN v_3; $K=$				ODD v_3; $K=$			
			Σ^+_u	Σ^-_u	Π_g	Δ_u	Φ_g	Σ^+_g	Σ^-_g	Π_u	Δ_g	Φ_u	0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
${}^e\Sigma^+_g$	v_3 even:	Σ^+_g	η							p			$\boldsymbol{\eta}$					ζ								ξ		
		Π_u			η			p	p		p			$\boldsymbol{\eta}$			ζ		ζ			η			ξ		ξ	
		Δ_g				η				p		p			$\boldsymbol{\eta}$			ζ		ζ			η			ξ		ξ
		Φ_u					η				p					$\boldsymbol{\eta}$			ζ					η			ξ	
	v_3 odd:	Σ^+_u			p			η									$\boldsymbol{\eta}$					ξ						

rather near together. Reasons why a bent upper state is likely have been given earlier.[6]

In connection with Liebermann's analysis of some of the bands of this system,[7] it was desirable to determine what selection rules and band structures are expected for (a) linear ${}^{e1}\Sigma^+_g \rightarrow$ linear ${}^{e1}\Pi_g$; (b) linear ${}^{e1}\Sigma^+_g \rightarrow$ bent ${}^{e1}A_2$ and ${}^{e1}B_2$. The results of this study are also of general interest.

Kusch and Loomis's observation of bands of this system in the form of a magnetic rotation spectrum[8] indicated the existence of a magnetic moment along the figure axis in the upper electronic state. This would call for a P, Q, R band structure, however. Since the bands actually have P, R structure, the magnetic moment must be directed along the J vector, and must be of secondary origin, like that in the visible iodine bands. The existence of magnetic rotation is, therefore, not decisive as to the linearity or non-linearity of the molecule in the upper state. Hence let us consider the two possibilities in succession.

The transition ${}^{e1}\Pi_g$, ${}^{e1}\Sigma^+_g$ in a *linear* molecule is forbidden by the electronic selection rules, but its appearance with rather low intensity (such as is observed) would not be unreasonable. Any well-developed bands must, however, obey the vibronic selection rules. Table II (sections 1–2) shows all the allowed kinds of bands, with their polarization, for various types of upper and lower vibronic states. Parallel (η) and perpendicular (p) bands are both possible. They should have, respectively, the same structures as like-designated diatomic molecule bands.

At room temperature, the most prominent absorption bands should arise from the vibrationless lower state, of vibronic species ${}^1\Sigma^+_g$. Parallel bands ($\Delta J = \pm 1$) going to ${}^1\Sigma^+_u$ upper vibronic states, and perpendicular bands ($\Delta J = 0, \pm 1$) going to ${}^1\Pi_u$ upper states, are here possible (see Table II). For the former, the most probable upper states are those with $v'_3 = 0$, $v'_\rho = 0$, $l' = 1$, for the latter, those with $v'_3 = 1$, $v'_\rho = l' = 0$. Changes in v_1 should be governed by the Franck-Condon principle. Weak bands involving multiples of $2\nu_2$ and $2\nu_3$ are also possible.

Less prominent absorption bands should arise from vibrating lower states. For the lowest such state ($v''_3 = v''_1 = v''_\rho = 0$, $l'' = 1$), of vibronic species ${}^1\Pi_u$ (cf. Fig. 1), the most favored upper vibronic states should be the ${}^1\Pi_g$ states with $v'_3 = v'_\rho = l' = 0$ in the case of parallel bands ($\Delta J = 0, \pm 1$), and the ${}^1\Sigma^+_g$, ${}^1\Sigma^-_g$, and ${}^1\Delta_g$ states with $v'_3 = 1$, $v'_\rho = 0$, $l' = 1$ in the case of perpendicular bands.

The right-hand half of Table II corresponds to a *bent* upper state. Here some of the vibronic transitions with η polarization, belonging to ${}^{e1}B_2$, ${}^{e1}\Sigma^+_g$, may be called electronic-allowed, although strictly this is justified only in emission where the initial state is bent, but not in absorption where it is linear. There are also several types of electronic-forbidden transitions, of both the parallel (η) and perpendicular (ξ or ζ) kinds, going to both ${}^{e1}B_2$ and ${}^{e1}A_2$ upper states.

Table II and Fig. 1 form a useful guide in the attempt to interpret the observed CS_2 absorption bands. In connection with Fig. 1, it is to be noted that if the upper equilibrium configuration is bent, the two upper electronic states ${}^1A_2$ and ${}^1B_2$ must differ in equilibrium dimensions and energy.

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[7] L. Liebermann, Phys. Rev. **60**, 496 (1941), (this issue, preceding paper).

[8] P. Kusch and F. W. Loomis, Phys. Rev. **55**, 850 (1939).

Unpublished considerations on the electronic structure of CS_2 indicate, for that molecule, somewhat greater bending at equilibrium and a lower energy minimum for the ${}^1B_2$ than for the ${}^1A_2$, and Fig. 1 has been constructed accordingly.

For a bent upper state, the most probable transitions from the vibrationless lower state, on the basis of Table II and the Franck-Condon principle, are parallel transitions to levels $v'_3=0, K'=0$ of ${}^{e1}B_2$ and perpendicular transitions to $v'_3=1$, $K'=1$ of ${}^{e1}B_2$ and ${}^{e1}A_2$. The most probable values of v'_2 should be large. Only one value of K'' and K' is involved for each band. Hence, unlike typical symmetrical-top bands where both J and K structures are present, each band should show only a structure due to J. Since, even for a considerably bent CS_2 molecule, there is little deviation from the linear-molecule rotational energy formula $BJ(J+1)+\cdots$,[7] the band structures should be practically indistinguishable from those of linear or diatomic molecules.

In the case that $K'=1$, there should be an appreciable splitting of the upper rotational levels due to asymmetry, so as to give effectively two values of B', one for the Q branch, the other for the P and R branches, as in Λ-doubling in diatomic molecules. For an adequately resolved structure, the sign and magnitude of the difference in the two B's could be obtained. The *sign* would show whether the transition is to ${}^{e1}A_2$ or ${}^{e1}B_2$ (cf. Fig. 6 of preceding paper,[1] for $K=1$); the *magnitude*, in conjunction with energy formulas of asymmetric-top theory, would show (provided perturbations between ${}^eA_2$ and ${}^eB_2$ are small enough) just how much the molecule is bent.

For bands arising from a vibrating lower state (cf. Table II), there is again just one value of K'' and of K' for each band, and the structures should again be practically identical with those of linear molecules; or at most there are two values of K', which should give an appearance like two linear-molecule bands close together or overlapping. From the lowest vibrating state ($K''=1$, ${}^1\Pi_u$ vibronic state), parallel-type transitions can occur to ${}^{e1}B_2$ and ${}^{e1}A_2$ levels with $K'=1$, $v'_3=0$ (or v'_3 even). Perpendicular bands can also occur, going to levels $K'=0$ and 2, $v'_3=1$ (or odd), of the ${}^eB_2$ and ${}^eA_2$ states.

All of the analyzed CS_2 bands are parallel bands of the P, R branch type ($K'=K''=0$). Within the errors of measurement, the structures of all these bands agree with what is expected for the case of a linear upper state; but as Liebermann has shown, the asymmetric-top corrections are so small for $K'=0$ that the data are equally consistent with an upper state with apex angle as small as 125°. There is no definite evidence of perpendicular bands in the spectrum. (It should, however, be kept in mind that only bands in the weak long wave-length end of the spectrum have been studied as yet.)

The simplest interpretation of the observed spectrum is that it actually corresponds chiefly to the allowed electronic transition ${}^1B_2-{}^1\Sigma^+_g$. This is confirmed by several features in the vibrational structure. In the long wave-length part of the spectrum, the Franck-Condon principle for a bent upper level favors transitions from states in which ν_2 is initially excited; and in fact Liebermann has analyzed three such bands, arising from the level $2\nu_2$; these bands are much stronger than the Boltzmann factor for $2\nu_2$, alone, would permit. Further, a long vibrational progression with $\Delta\nu$ about 270 cm^{-1}, observed by various authors and clarified by Liebermann, can hardly be interpreted otherwise than as a ν'_2 progression of a bent molecule. For 270 cm^{-1} is definitely too small for ν'_1, in view of the fact (cf. Eqs. (6), (7)) that only one electron has jumped while eight bonding electrons remain; and a possible identification of 270 cm^{-1} with $2\nu'_2$ of a linear molecule is incompatible with the Franck-Condon principle, since the 270 cm^{-1} progression is too long, and has an intensity maximum.[7] The large total number of observed bands in the spectrum can now reasonably be attributed to extensive progressions in both ν'_1 and ν'_2 and combinations of these, assuming a bent upper state. As Liebermann has shown, the observed values of B' correspond to a considerable increase of r' over r'' *provided* the molecule is considerably bent in the upper state. The Franck-Condon principle would then call for extensive excitation of ν'_1. Thus an allowed ${}^1B_2$, ${}^1\Sigma^+_g$ electronic transition to a bent upper state seems to be established.

This is in agreement with the writer's earlier expectations. These, however, call for additional, presumably weaker, vibronic-allowed transitions to the $^1B_2$ and to a closely adjacent $^1A_2$ upper electronic state. These and other electronic-forbidden bands may well be present among the very numerous bands not yet analyzed.

It is interesting to inquire somewhat into the factors governing the intensity of the observed electronic transition $^1B_2$, $^1\Sigma^+{}_g$. The normal electron configuration and state of CS_2 may be written as follows:[9]

$$\cdots(\sigma s\sigma,\ \sigma_g)^2(\sigma 0\bar{\sigma},\ \sigma_u)^2(\pi\pi\pi,\ \pi_u)^4(\pi 0\bar{\pi},\ \pi_g)^4 \times(\sigma\bar{s}\sigma,\ \sigma_g)^0(\bar{\sigma}\sigma\sigma,\ \sigma_u)^0(\pi\bar{\pi}\pi,\ \pi_u)^0,\ {}^1\Sigma^+{}_g. \quad (6)$$

The *MO*'s with superscript zero are unoccupied but capable of being occupied in excited states. We shall be interested in two such electronic states:

$$(\pi 0\bar{\pi})^3(\sigma\bar{s}\sigma)^1,\ {}^1\Pi_g;\quad (\pi 0\bar{\pi})^3(\pi\bar{\pi}\pi)^1,\ {}^1\Sigma^+{}_u. \quad (7)$$

In (7) all *MO*'s not mentioned are supposed to be populated in the same way as in (6).

For a linear molecule, the electronic transition to the $^1\Pi_g$ of (7) is forbidden, but that to the $^1\Sigma^+{}_u$ is allowed, and *strongly* so, since it is easily seen that the transition involved ($\pi 0\bar{\pi}\rightarrow\pi\bar{\pi}\pi$) has $N\rightarrow V$ characteristics.[10] (The strong CS_2 bands near $\lambda 2000$ are, perhaps, to be identified with this transition.)

Now consider, for a linear molecule, vibrating states of the $^{e1}\Pi_g$ state such as to give $^1\Sigma^+{}_u$ vibronic states. (Such a state can be obtained, for example, if one quantum of ν_2 is excited.) These $^1\Sigma^+{}_u$ vibronic states will be perturbed by the $^1\Sigma^+{}_u$ electronic state of (7). Vibronic perturbations such as these will overcome the complete forbiddenness of the $^1\Pi_g$, $^1\Sigma^+{}_g$ electronic transition, giving *P*, *R* bands which might even have considerable intensity and explain the observed CS_2 bands.

However, suppose the molecule is bent in its upper electronic state. The $^{e1}\Pi_g$ then splits into $^{e1}B_2$ and $^{e1}A_2$ and the $^{e1}\Sigma^+{}_u$ becomes $^{e1}B_2$. As the molecule becomes bent, the two $^{e1}B_2$ wave functions begin to mix, and thus the transition to the $^{e1}B_2$ derived from $^{e1}\Pi_g$ becomes more and more allowed. [Of course other higher $^{e1}B_2$ wave functions also mix in, but it is improbable that any of them are important for the intensity.] It is easily shown, using perturbation theory, that the extent of mixing should be proportional to the amount of bending. However, as a result of the fact that the molecule is linear in its lower electronic state, it is found that the *total* absorption intensity for an upper state of the kind here considered should be just the same whether the equilibrium configuration of the upper state is bent or linear. Thus in either case our analysis indicates that the intensity of the observed bands may be attributed mainly to the influence of the $^{e1}\Sigma^+{}_u$ state of (7).

The Franck-Condon principle can now be applied. For an upper state with bent equilibrium configuration, the usual Franck viewpoint applies and predicts that the strongest bands should involve excitation of ν'_2, together with perhaps a few quanta of ν'_1, with enough energy to carry the excited molecule from its bent equilibrium state up to a practically linear configuration[11] (not quite linear, when one corrects for the forbiddenness of the transition in an exactly linear molecule). Further, the *total* intensity of all the absorption bands from any given initial vibrational state should increase strongly (with of course some shift in the intensity distribution among upper vibrational states) if the bending vibration is excited in the lower state. A preliminary examination of the intensity integrals involved indicates proportionality of the total intensity to v''_2+1. [Experimental confirmation of this prediction would not, however, give evidence for or against a bent upper equilibrium state, since the *same* prediction is found to be valid for a linear upper state.]

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[9] This is based on Eqs. (16a), (17) of reference 6, with some simplication in the *LCAO* notation.

[10] Cf. R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939), in regard to $N\rightarrow V$ transitions.

[11] That is, the Franck principle would say that, at the first instant after the transition, the molecule should be linear. This would then have to correspond to the large angle phase of a violent angular vibration. It is to be noted that such a motion, if $K>0$, would involve very strong rotation-vibration interaction, leading to an irregular arrangement of energy levels (cf., earlier parts of this paper).